

## **Effect of caffeic acid adsorption in controlling the morphology of gold nanoparticles: role of surface coverage and functional group**

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### ***Supplementary Information***

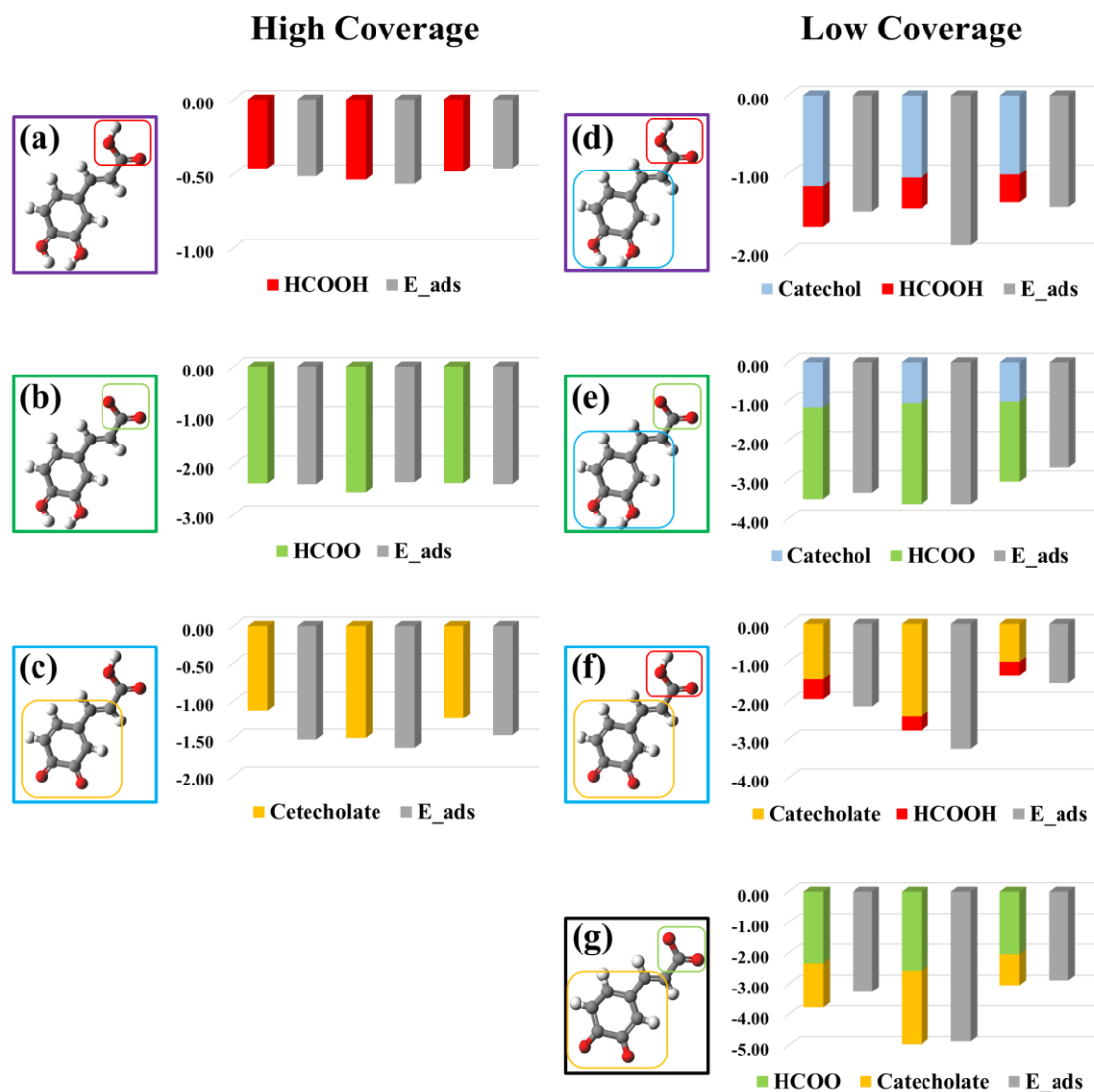
We calculated the adsorption energies of caffeic acid (CA) and its functional groups on Au (100), (110) and (111) surfaces to examine the contribution of each functional group to the molecular adsorption strength. We selected four types of functional groups based upon the adsorption configuration of CA and deprotonated CA molecules in Figs. 2, 3. Our results showed that two functional groups among -COO, -COOH, -C<sub>6</sub>H<sub>4</sub>O<sub>2</sub> (catecholate) and -C<sub>6</sub>H<sub>6</sub>O<sub>2</sub> (catechol) are involved in molecular adsorption at low coverage whereas only one of -COO, -COOH or -C<sub>6</sub>H<sub>4</sub>O<sub>2</sub> participates in the adsorption at high coverage. The adsorption strength of catechol has little dependence on the different surface structures of Au(100), (110) and (111). However, it can be changed by the deprotonation on each surface. (Tables S1 and S2).

|       | F1    | F2   | E_ads | E_sum |
|-------|-------|--|-------|-------|
| CA    | HCOOH | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> |       |       |
| 100   | -0.51 | -1.16  | -1.48 | -1.67 |
| 110   | -0.39 | -1.05  | -1.91 | -1.44 |
| 111   | -0.35 | -1.01  | -1.42 | -1.36 |
| CA-H  | HCOO  | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> |       |       |
| 100   | -2.33 | -1.16  | -3.33 | -3.49 |
| 110   | -2.57 | -1.05  | -3.62 | -3.62 |
| 111   | -2.04 | -1.01  | -2.69 | -3.05 |
| CA-2H | HCOOH | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> |       |       |
| 100   | -0.51 | -1.44  | -2.14 | -1.95 |
| 110   | -0.39 | -2.39  | -3.25 | -2.78 |
| 111   | -0.35 | -1.00  | -1.54 | -1.35 |
| CA-3H | HCOO  | C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> |       |       |
| 100   | -2.33 | -1.44  | -3.26 | -3.77 |
| 110   | -2.57 | -2.39  | -4.86 | -4.96 |
| 111   | -2.04 | -1.00  | -2.88 | -3.04 |

**Table S1:** Calculated adsorption energies of CA and the deprotonated CA at low coverage. F1 and F2 indicate the adsorption energy of representative of the functional group involved in the molecular adsorption.

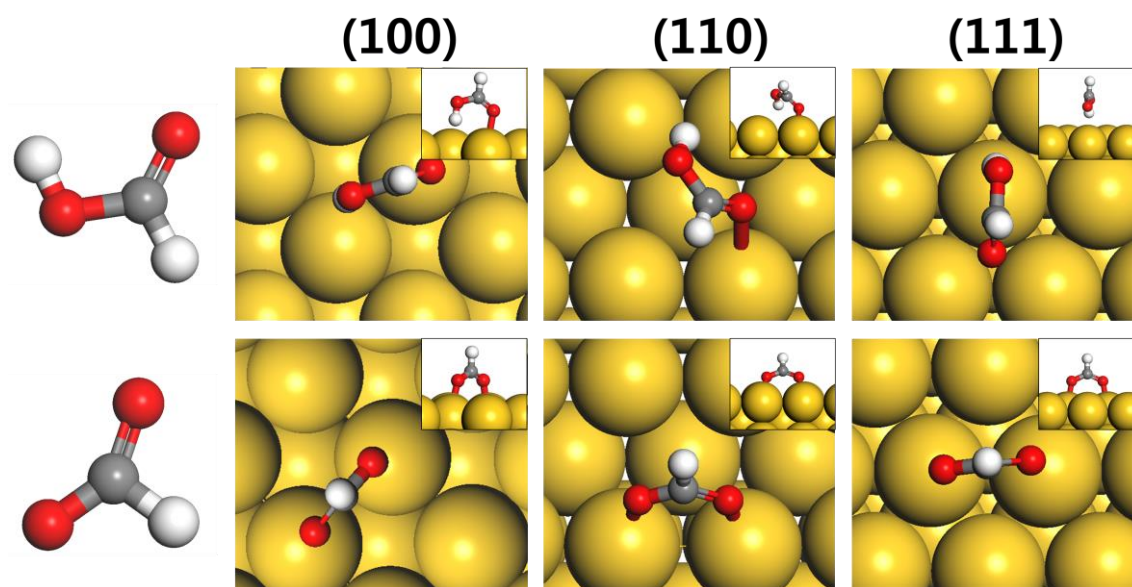
|       | F1   | F2   | E_ads | E_sum |
|-------|--|--|-------|-------|
| CA    | HCOOH  | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> |       |       |
| 100   | -0.46  | -  | -0.52 | -0.46 |
| 110   | -0.54  | -  | -0.57 | -0.54 |
| 111   | -0.48  | -  | -0.46 | -0.48 |
| CA-H  | HCOO   | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> |       |       |
| 100   | -2.37  | -  | -2.38 | -2.37 |
| 110   | -2.55  | -  | -2.34 | -2.55 |
| 111   | -2.36  | -  | -2.38 | -2.36 |
| CA-2H | C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> | HCOOH  |       |       |
| 100   | -1.13  | -  | -1.52 | -1.13 |
| 110   | -1.5   | -  | -1.63 | -1.50 |
| 111   | -1.24  | -  | -1.46 | -1.24 |

**Table S2:** Calculated adsorption energies of CA and the deprotonated CA at high coverage. F1 and F2 indicate the adsorption energy of representative of the functional group involved in the molecular adsorption.



**Figure S1:** Comparison of the adsorption energies of CA and the deprotonated forms calculated by DFT with the estimated values from our prediction model for functional group contribution at each coverage. Contrary to the low coverage, only one functional group can be involved in the molecular adsorption at high coverage due to the limitation of adsorption configuration. Each functional group is highlighted to red, green, orange and blue rectangular boxes, respectively.

In our manuscript, significant deviation for CA adsorbed at the low coverage of Au(100) is observed due to the discrepancy of adsorption geometries between CA and the functional group-derived molecules. Since carboxyl group is closely involved in molecular adsorption of CA, we analyzed the adsorption geometry of formic acid and its deprotonated form (formate). At high coverage, the adsorption configurations of formic acid (HCOOH) and formate (COOH) (Fig. S2) are similar to those of CA and the deprotonated forms through the terminated oxygen and hydroxyl group (Fig. 3). On the other hand, at low coverage, the aromatic carbon atoms in CA and the deprotonated forms additionally participate in the molecular adsorption via van der Waals interactions (Fig. 3).



**Figure S2:** Top views of the adsorption structures of formic acid (up) and formate (down) on Au(100), (110) and (111), respectively.